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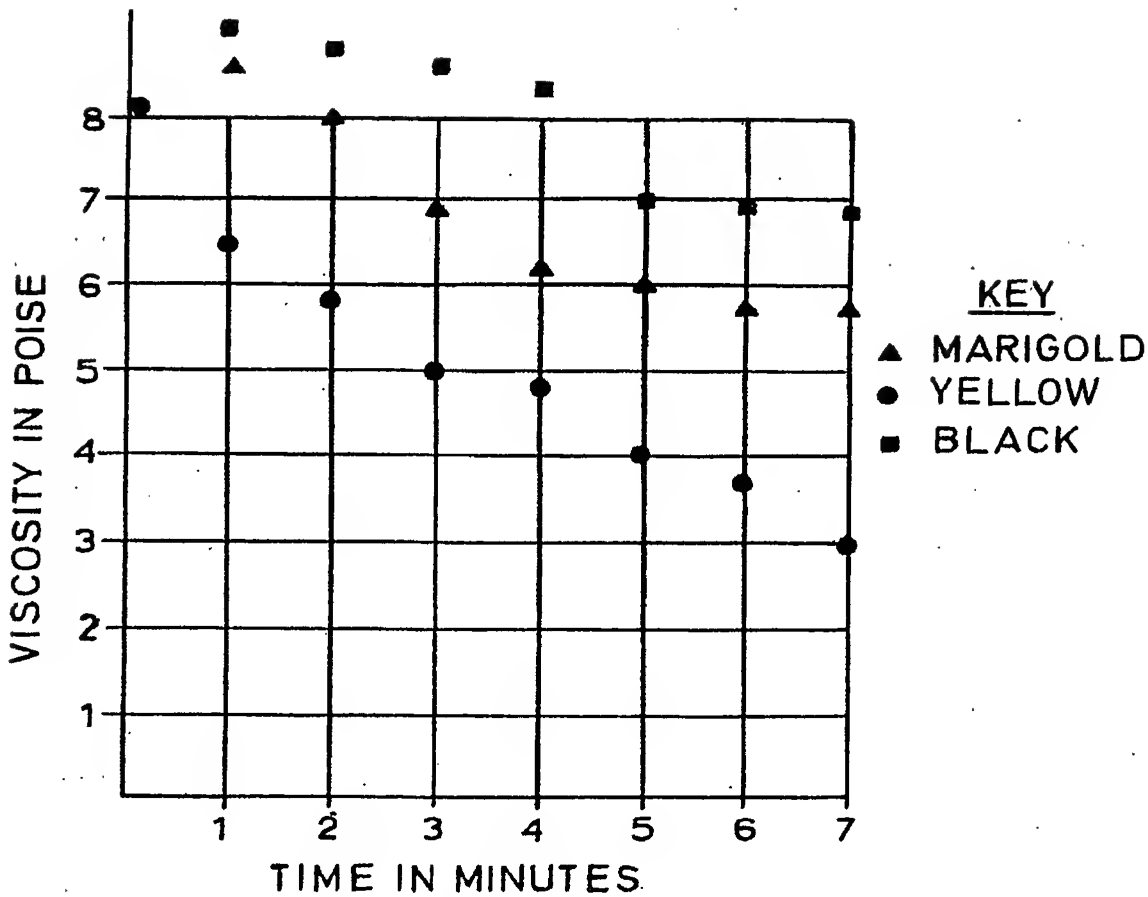
(54) Method of Producing Cement Colouring Composition

(57) A thixotropic slurry is made by first mixing a dispersant (preferably 0.1 to 3%, based on the weight of slurry), a stabilizer (preferably 0.4 to 15%), and an aqueous carrier (preferably 12 to 77%), then mixing in a solid particulate pigment (preferably 20 to 70%) until the resulting mixture is uniform, and finally subjecting the mixture to high energy processing, e.g. milling, to reduce the pigment particles to a micron size range, preferably 0.5 to 40 microns.

The drawing originally filed was informal and the print here reproduced is taken from a later filed formal copy.


8
7
6
5
4
3
2
1
VISCOSITY IN POISE
1
2
3
4
5
6
7
TIME IN MINUTES
KEY
MARIGOLD
YELLOW
BLACK

SPECIFICATION
Method of Producing Cement Colouring Composition

This invention relates to a method of producing a colouring material for cementitious mixes used in making products such as cast concrete, extruded concrete, cement fibre glass, and cement asbestos.

Conventional cement or concrete colouring compositions comprise powders which are added by hand or by a screw conveyor in their dry state to a wet concrete or cement mix in a mixing apparatus. It is difficult to accurately add desired amounts of such powders to the wet concrete mix and there is often waste of such colouring material. Furthermore, with powders it is difficult to obtain a sufficient thorough mixing of the powders into the wet cement mix so as to achieve a homogeneous colour throughout the mixture. Conventional methods also require the concrete or cement contractor to maintain large inventories of the colouring composition and involve certain health hazards as well.

It is highly desirable to have a system for colouring wet cement and concrete mixes by the addition of the colouring material in a liquid form to the mix, so that the colouring material may be added by liquid pumps to the wet concrete mix. In particular it is desirable to be able to produce a pigment suspension which will not settle out within a relatively short time.

The present invention provides a method of producing a colouring composition for a cementitious mix, comprising making a thixotropic slurry by the following steps: (a) forming a mixture of a dispersant and a stabilizer in an aqueous carrier; (b) mixing a solid particulate pigment into the mixture from step (a) until the resulting mixture is uniform; and (c) subjecting the mixture from step (b) to high energy processing which reduces the pigment particles to a micron size range.

Preferably, the following amounts of the dispersant, the stabilizer, the aqueous carrier, and the pigment are used, based on the weight of the slurry: dispersent, 0.1 to 3%; stabilizer, 0.4 to 15%; aqueous carrier, 12 to 77%; pigment, 20 to 70%.

The invention will be described further with reference to the following Examples and the accompanying drawing, whose sole Figure is a graph illustrating preferred ranges of viscosity plotted against time for three exemplary iron oxide pigments after they have been processed into slurries.

In the following description all percentages are by weight.

Example 1

A mixing tank having a slow speed or low energy agitator revolving at 80 to 200 rev/min is partially filled with 47.17% of water (based on the weight of slurry to be produced). A natural gum such as gum arabic in the amount of 5% is then added as well as 0.66% of a dispersant such as sodium laurate, which is a sodium salt of lauric acid sulphonate. At ambient temperatures, the water, dispersant, and stabilizer are premixed until all are dissolved. Then, while the mixer is still running, 47.17% of a pigment such as black iron oxide is added and the entire mixture is then mixed for about one hour, for example, until it is uniform and homogeneous, whereupon it will have a predetermined specific gravity.

Next, the material is pumped into a high speed or high energy mill such as a stone mill, for example, to reduce the particle size of the pigment component of the slurry down into the micron range. This can be checked by the use of a grinding "wedge" or other gauge. Preferably, the pigment particle size distribution in the resulting thixotropic slurry should include largest particles with a maximum dimension of about 40 microns, large particles whose average size is about 25 microns, smaller particles whose average size is in the 1—2 micron range, and smallest particles down to a minimum size of about 0.5 microns. If the particle distribution is generally higher than these ranges, the colouring strength of the slurry is adversely affected. If the sizes of the particles are generally below these ranges they may be washed out of dried concrete by normal weathering.

The procedure described above may also be applied to many other formulations such as are set forth in the following examples:

Example 2

Black Iron Oxide	47.17%
Water	47.73%
Gum Arabic	5.00%
Sodium Laurate	0.10%

Example 3

Carbon Black	20.00%
Water	76.60%
Gum Arabic	0.4%
Ethylene Oxide Condensate	3.0%

Example 4

Carbon Black	25.0%
Water	59.0%
Alginate L.V.	15.0%
Sodium Laurate	1.0%

Example 5

Spanish Red Oxide	80.0%
Water	12.69%
Gum Arabic	7.0%
Ethylene Oxide Condensate	0.4%

Example 6

Red Oxide (Natural)	60.00%
Water	30.00%
Gum Arabic	9.20%
Sodium Laurate	0.80%

Example 7

Red Oxide (Synthetic)	50.00%
Water	47.00%
Gum Arabic	2.80%
Sodium Laurate	0.20%

Example 8

Yellow Oxide (Synthetic)	47.00%
Water	49.5%
Gum Arabic	3.2%
Sodium Laurate	0.3%

Example 9

Yellow Oxide (Synthetic)	47.00%
Water	49.5%
Sodium Alginate (Manute RS)	3.2%
Sodium Laurate	0.3%

Example 10

Yellow Oxide (Synthetic)	47.00%
Water	49.5%
Carboxymethyl Cellulose (CMC) High Viscosity grade	3.2%
Sodium Laurate	0.3%

Example 11

Yellow Oxide (Synthetic)	47.00%
Water	49.5%
Gum Arabic	3.4%
Triethanolame	0.1%

Example 12

Yellow Oxide (Synthetic)	47.00%
Water	49.5%
Gum Guar	3.2%
Sodium Laurate	0.3%

Example 13

Yellow Oxide (Synthetic)	47.00%
Water	49.5%
Gum Tragacanth	3.2%
Sodium Laurate	0.3%

Example 14

Yellow Oxide (Synthetic)	47.00%
Water	49.5%
Locust Bean Gum	3.2%
Sodium Laurate	0.3%

Example 15

Yellow Oxide (Synthetic)	47.00%
Water	49.5%
Dextrine	3.2%
Sodium Laurate	0.3%

Example 16

Yellow Oxide (Synthetic)	47.00%
Water	49.5%
Potato Starch	3.2%
Sodium Laurate	0.3%

Example 17

Yellow Oxide (Synthetic)	47.00%
Water	49.5%
Polyvinyl Alcohol	3.2%
Sodium Laurate	0.3%

Example 18

Yellow Oxide (Synthetic)	47.00%
Water	49.5%
Polyvinyl Pyrolidone	3.2%
Sodium Laurate	0.3%

The dispersant helps the slurry to keep its suspended state for long periods of time, and they facilitate the incorporation of large amounts of pigment into the slurry. They also tend to prevent flocculation of the pigment when the slurry is added to a cement mix containing free calcium ions. Less flocculation makes for more intense colouring of the cement mix.

In each of the above examples the water may be replaced by an aqueous solution of a freezing point depressant in such an amount that the slurry freezes only below a given subzero temperature.

By way of example, in order to achieve a freezing point of −25°C, any one of the following freezing point depressants can be used in the following percentages based on the quantity of aqueous solution: magnesium sulphate 25%; sodium sulphate 25%; ethylene glycol 15%; propylene glycol 17%; glycerol 20%; sorbitol 20%; ethyl alcohol 30%; methyl alcohol 33%; isopropyl alcohol 33%. Magnesium and sodium sulphate have a slight retarding effect on the curing of the cementitious products. The alcohols appear not to affect curing, even when used at high concentrations, e.g. 8 to 10% based on the weight of the cementitious mix.

In practice the amount of freezing point depressant may be such that the slurry freezes only below −5°C, preferably only below −10°C. The amount is preferably 5 to 35% based on the weight of the aqueous solution.

It has been found that without the freezing point depressant the storage life of the slurry is sometimes shorter than expected. It is believed that this is owing to the effect of low temperatures when storage extends into winter. The inclusion of the freezing point depressant brings an improvement in storage life which appears to be due not only to the lower freezing point but also to the fact that, if the slurry does freeze, the way in which it freezes (passing through a paste-like state) inhibits settling out.

It is important that the viscosity of the formulation be controlled so as to ensure that the formulation can be fluidized when being dispensed, thereby to optimize the mixing of the formulation with the cement or concrete components. The product is therefore checked as to its viscosity, which should fall substantially within the limits (measured in poise) as shown in the accompanying drawing. While the data shown in the graph just deals with iron oxides, the desirable viscosity ranges for other pigments will also fall within the maximum and minimum ranges shown in the graph. The data plotted was determined by the use of a "Rotothinner" brand viscometer manufactured by ICI. This viscometer

works by detecting mechanical shear, not by the detection of heat generation.

The colour quality of the slurry may be tested by adding to it a predetermined quantity of titanium dioxide (white) in the 3:1 to 5:1 ratio range. This measures the relative value of the colour, since a given sample may require a different amount of the colouring pigment to produce the same tint as another betch of the slurry.

Other usable stabilizers include active clays such as bentonite, kieselgur, or benagel, uncooked corn or wheat starch, water-soluble celluloses such as hydroxy ethyl cellulose or methyl cellulose, and polyvinyl pyrolidone.

Other usable dispersants include other fatty amines and alkylamines. Cationic surfactants, such as "Wetfix SE" (trade merk), are particularly suiteble for compositions to be used for colouring cement asbestos.

Optionally, other substances may also be added to impart desired characteristics to the composition. For example, a small percentage, say 4 to 7%, of an anti-efflorescence agent such as barium carbonate can be added. Or small percentages (say about 2%) of water-repellent chemicals such as calcium stearate, aluminium stearate, or silicones cen be added to the pre-mix of the dispersant and the stabilizer in the aqueous carrier.

The premixing step may be alternatively accomplished by using a hydraulic, variable speed cavitation mixer such as those marketed by Torrance & Sons of Bristol, England, or by Cowles in the United States. Present cavitation mixers are, however, somewhat limited in processing capacity.

The reduction of the particle size of the original slurry by high energy processing may be done by mills other than the stone mill. Alternatively, a Premier brand colloid mill manufactured by Premier Colloid Mills or other types of comminuting apparatus may be employed. Stone mills may be those menufactured by Moorhouse in the United States or by Fryma In Switzerland. Ball mills or rod mills have also been satisfactorily used, but they have the disadvantage of requiring more processing time. Attrition mills such as sand mills or pearl mills also ere effective, but also usually take longer than high speed mills or colloid mills.

One of the main advantages of the present invention is that thixotropic slurries of various main colours produced according to the present invention may be packaged in drums or other containers and the suspensions will not settle out for reletively long periods of time, i.e. of the order of 6 to 12 months. Thus, if the concrete or cement contractor wishes, he can keep perhaps 3 to 5 pigment slurries in individual drums, each slurry being operatively connected to a batching system which controls the amounts of the slurries to be added to the concrete mix. A charging pump may be inserted into each drum of slurry connected through a delivery tube to a metering container or tube. The tube may, for example, contain a first (higher) measuring probe connected to a batching control unit whose height is adjustable (or predetermined) depending upon the amount of slurry to be measured out. Operation of the charging pump delivers the slurry to the metering tube until it touches the lower end of the first measuring probe whereupon a circuit is actuated which cuts off the pump. The charging pump for applying the slurry to the metering tube may be an air-operated positive displacement piston pump such as those marketed by Graco, Inc. of Minneapolis, Minnesota. Then the contents of the metering tube start to be withdrawn from the metering tube by the action of a dispensing pump (controlled by the batching unit) and to be applied (with water) to a concrete mixer of any conventional type. When the level of the metered slurry falls below the lower end of a second probe coupled to the batching unit, a signal is generated which stops the dispensing pump.

If the contents of the slurry drum have not been used for excessive lengths of time, it may be advisable to insert a recycling valve branching off from the output of the charging pump and being connected to a recycling tube which returns to the drum. The return of the slurry beck to the drum will produce a certain amount of agitation of the contents of the drum.

Instead of the batching system described above, it is also possible to use a positive displacement pump of the said Graco type or of the "Mono" brand type marketed by Mono Pumps Ltd. of Great Britain. The latter pump is also marketed in the United States under the "Moyno" brand by Robbins and Meyers. The pump is set to run for a timed period so thet, since the rate of flow is known, the amount of pumping time required to produce a given volume can easily be calculated. The timers may be wired to the electric motor starters of the pumps.

Still another method is to pump the slurry around a continuous circuit *via* a three-way valve which is air or electrically operated. The valve is connected to a timer that can switch it from continuous circuit to injection by-pess, either straight into the mixing apparatus or indirectly, *via* a weighing scale, into the mixer so as to provide a double check on the quantity required for addition.

Claims

1. A method of producing e colouring composition for a cementitious mix, comprising making e thixotropic slurry by the following steps:

(a) forming a mixture of a dispersant and a stabilizer in an aqueous carrier;

(b) mixing a solid particulate pigment into the mixture from step (a) until the resulting mixture is uniform; and

(c) subjecting the mixture from step (b) to high energy processing which reduces the pigment particles to a micron size range.

2. A method as claimed in claim 1, in which the following amounts of the dispersant, the stabilizer,

the aqueous carrier, and the pigment are used, based on the weight of the slurry: dispersant, 0.1 to 3%; stabilizer, 0.4 to 15%; aqueous carrier, 12 to 77%; pigment, 20 to 70%.

3. A method as claimed in claim 1 or 2, in which the stabilizer comprises at least one of the following: active clays, natural products of the alginate group, hydrolysed starches, water-soluble celluloses, natural starches, synthetic polymers of the polyvinyl type, and water-soluble natural gums.

4. A method as claimed in any of claims 1 to 3, in which the pigment comprises at least one of the following: metallic oxides, metallic salts, and carbon black.

5. A method as claimed in any of claims 1 to 4, in which the pigment particle sizes are substantially within the range 0.5 to 40 microns.

6. A method as claimed in any of claims 1 to 5, in which the dispersant comprises at least one of the following: ethylene oxide condensates, fatty amines, alkylamines, and sulfonated soaps in the form of a metal derivative salt.

7. A method as claimed in any of claims 1 to 5, for producing a composition for colouring cement asbestos, in which the dispersant is a cationic surfactant.

8. A method as claimed in any of claims 1 to 7, in which the aqueous carrier is water.

9. A method as claimed in any of claims 1 to 7, in which the aqueous carrier contains a freezing point depressant in such an amount that the slurry freezes only below −5°C.

10. A method as claimed in claim 9, in which the amount of freezing point depressant is such that the slurry freezes only below −10°C.

11. A method as claimed in claim 9 or 10, in which the aqueous carrier contains 5 to 35% by weight of the freezing point depressant.

12. A method as claimed in any of claims 1 to 11, in which the freezing point depressant comprises an alcohol.

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